10/582349
IAP20 Rec'd PCT/PTO 09 JUN 2006

WO 2005/061081

PCT/EP2004/010434

poromedia GmbH, Böblinger Str. 160, 70199 Stuttgart

Method for the production of tubular membranes

The invention relates to a method for the production of tubular membranes.

EP 0 349 914 B1 discloses a method for the production of tubular nonwoven fabric articles from a strip of a thermoplastic nonwoven support which, in order to form a nonwoven tube, is wound up in a spiral form in such a way that the longitudinal edges of the strip overlap along a joining seam, at least in the wound area of the nonwoven tube, this joining seam being formed by thermally welding the longitudinal edges to one another. Winding the strip up into the spiral nonwoven article results in the creation of a hollow rod which, at its free end, has an outlet opening through which a coating solution can be applied to the inside wall of the wound nonwoven tube, and, by subsequent contact with a coagulation solution, a tubular membrane is obtained.

Tubular membranes of this kind are suitable in particular for ultrafiltration and nanofiltration, the membranes in question forming microporous filter media whose pores are so small that they form a barrier not only to particles of all kinds and shapes, such as pollutants, heavy metals, etc., but also to all microorganisms, for example in the form of bacteria, parasites and viruses. The active layer of the membranes is also referred to in the technical field as the semipermeable layer. A disadvantage of tubular membranes produced in this way is that, under the pressure exerted by the liquid that is to be filtered, they often tear in the area of the thermal connecting seams and thus fail to function properly. To counteract this, the German laid-open specification 2 255 989 has already proposed that the outside periphery of the

semipermeable membrane tubes, which are also thin and fragile, should be enclosed by a reinforcement in the form of a braided fiber structure in order to counter the high hydraulic internal pressure; however, the known production method is complicated and therefore expensive, and the reinforcement in the form of the braided fiber structure that bears directly on the semipermeable membrane has a disadvantageous effect on the rate of flow through the tubular membrane and on the latter's filtration properties.

To avoid the problems that arise when the pressure of a liquid causes undesired separation of the thermally produced connecting seams in a spirally wound tubular membrane made from a strip-shaped article, the document DE 199 09 930 A1 proposes a tubular composite structure composed of a braid of thread bundles and/or wires, preferably in the form of an electron-conducting material and, arranged over this, a layer of an ion-conducting material as fuel cell element. In this known solution, aimed among other things at producing what is known as a PEM fuel cell, it is proposed that the tubular inner electrode composed of carbon fibers and/or metal wires be produced by means of a braiding machine. This tubular braid is centered on a mandrel along which it runs as far as an applicator nozzle for the catalyst coating, the nozzle diameter defining the thickness of the catalyst coat. After a short drying section through ceramic heating elements, for example, the coated braid runs through an annular die via which the ion-conducting membrane is applied in the form of a polymer solution. This step is followed by a longer drying section for expelling the solvent. Thereafter, a second catalyst layer is applied by an applicator nozzle, and the outer electrode is then braided round the still pasty catalyst layer. The pasty consistency of the catalyst layer permits penetration of the braid strands and thus permits an intimate connection between catalyst and electrode. If this tubular composite

structure composed at least partially of a planar threaded braid is exposed to high pressures from liquids, it is not possible to rule out the possibility of the longitudinal and transverse tensile stresses in the braid causing the threads of the composite structure to shift relative to one another, which can result in undesired stretching effects, particularly in the production of the braid before the actual coating with the membrane material, the consequence of which is that the known tubular membrane adopts a shape, and in particular changes in diameter, such that it may be unsuitable for its subsequent intended purpose.

Starting out from this prior art, the object of the invention is to further improve the known technical methods for producing tubular membranes, in such a way that functionally reliable tubular membranes can be obtained at a high production rate and at low cost, and they do not suffer undesired stretching effects, with a change of membrane geometry, either during their production or in their subsequent use. This object is achieved by a method having the features of patent claim 1 in its entirety.

Since, in accordance with the characterizing part of patent claim 1, a tubular body is constructed from a plurality of threads in such a way that at least some of the threads are tied substantially firmly together along fillet-like connecting lines, that between the fillet-like connecting lines at least some of the threads form the transverse connection between the mutually adjacent connecting lines, and that a predefinable membrane material is applied to the tubular body, a very cost-effective production method is obtained with which it is possible to achieve very high output rates for tubular membranes. With the method according to the invention, it is possible, before application of the membrane material, to obtain tubular bodies in the manner of a conductive knit or

circular conductive knit, and the said conductive knit pattern means that any longitudinal tensile stresses that arise can be safely taken up by continuous longitudinal threads along the fillet-like connecting lines. The looping at the intersections of the conductive knit pattern, that is to say at the places where the connecting lines and said transverse connections are tied substantially firmly together, avoids shifting of the thread systems relative to one another, and the described adverse stretching effect during coating is minimized, so that the fabric-reinforced filtration capillary withstands very high internal pressures and mechanically applied longitudinal tensile forces.

In contrast to the braided tubular bodies in which the braid paths can shift relative to one another under corresponding stresses or loads, the looping at the places where the connecting lines and transverse connections are substantially firmly tied together means that shifting cannot take place, with the result that any longitudinal or transverse movements of the thread system are determined solely by the inherent elasticity of the thread material that is used. To this extent, the use of the method according to the invention results in tubular structures which have great dimensional stability and are stable to pressure, both during production of the membrane tubes and during the subsequent use thereof in the ultrafiltration or nanofiltration range of fluids of all types, including in the area of treatment of water and beverages.

In a particularly preferred embodiment of the method according to the invention, the tubular body designed as a conductive knit is created by means of a crocheting device, and each inserted thread is assigned its own hooked needle or crochet needle. Crocheting by nature is a needlework technique in which, with the aid of the hooked needle or crochet needle, the thread is

formed into loops "in the air", that is to say without a support, and the interlocking loops can be joined together to form patterns. With the crocheting device, it is possible to introduce supporting or retaining threads continuously along the fillet-like connecting lines, in order thereby to create a kind of base framework, and then to insert the further threads for the looping at the intersections along the connecting lines and produce the transverse thread arrangement between said connecting lines.

The tubular body is preferably created by crocheting in such a way that passages allowing liquid to pass through at a high flow rate are formed between the individual transverse connections, and that the fillet-like connecting lines are designed to be substantially liquid-tight or to allow liquid to flow through at a low flow rate. In a particularly preferred embodiment of the method according to the invention, said threads (monofilaments or multifilaments) are chosen from the group of

- synthetic materials such as polyester, polyaramides, other polymers, carbon, Kevlar, etc., or

- metals (wires) such as nickel, platinum, palladium, gold, silver, stainless steel, etc., or

- catalytically active substances such as ruthenium, rhodium, iridium, nickel, etc., or

- other materials such as cellulose acetate, glass fibers, graphite powder, activated charcoal, etc., or

from mixtures and compounds of the aforementioned groups.

The above list makes clear that within the meaning of the method according to the invention the word thread is to be interpreted broadly and, in addition to the usual monofilament and multifilament threads, also includes other linear elements such as yarns, wires or rod-like components, including ones constructed from powder.

The adjacent transverse connections are arranged between two connecting lines in such a way that between them they enclose an angle of 10 to 70°, preferably of approximately 25° to 45°, particularly preferably of 30°.

In another particularly preferred embodiment of the method according to the invention, the tubular body is coated with a membrane-activatable substance which is guided through a precipitation bath, the substance being converted into a microporous membrane layer.

The membrane materials are chosen in particular from the group of synthetic materials such as polyethersulfone (PES), polysulfone (PSU), polyacrylonitrile (PAN) or polyvinylidene fluoride (PVDF).

The method according to the invention is explained in more detail below on the basis of an illustrative embodiment and with reference to the drawing. The single figure shows in diagrammatic form, and not to scale, a perspective front view of a section of the tubular membrane in a much simplified representation.

In the method according to the invention for the production of tubular membranes, a tubular body designated overall by reference number 10 is constructed from a plurality of threads 12 in such a way that at least some of said threads 12 are tied substantially firmly together along fillet-like

connecting lines 14 and, between the fillet-like connecting lines 14, at least some of the threads 12 form the transverse connection 16 between the mutually adjacent connecting lines 14, and a predefinable membrane material 18 is applied to the tubular body 10. The fillet-like connecting lines 14 in this case form a kind of longitudinal thread system which, via the transverse threads 12 of the respective transverse connection 16, forms a kind of conductive knit, in particular a circular conductive knit.

To obtain the conductive knit in question, the tubular body 10 is created using an industrial crocheting device, each inserted thread being assigned its own hooked needle or crochet needle. Since mechanical crocheting devices of this kind belong to the prior art, the creation of the tubular body 10 by crocheting will not be dealt with in any further detail. In any event, the tubular body 10 is created by said crocheting in such a way that passages 20 allowing liquid to pass through at a high flow rate are formed between the individual transverse connections 16 in the form of the transverse threads 12, and the fillet-like connecting lines 14 acting as a longitudinal thread system are designed to be substantially liquid-tight or to allow liquid to flow through at a low flow rate. To make things clearer, the looping of the threads 12 of the transverse connections 16 with the fillet-like connecting lines 14 has been shown in the figure in the form of linking balls 22, while in reality the crocheting method means that the balls 22 in question are formed by interconnected stitches or knots, and the connecting stitches formed along the connecting lines 14 that cross over at both ends, that is to say to the right and left, to the threads 12 of the transverse connections 16, have additional longitudinal threads 12 which additionally increase the stability and the resistance to longitudinal tensioning of the tubular body 10.

The inserted threads 12 for the transverse connections 16 and for tying them to one another along the points 22 in the transition area to the fillet-like connecting lines 14 consist of multifilament synthetic threads, for example of polyester or polyaramides, although other polymers can also be used here. To increase the strength, however, the longitudinal threads along the fillet-like connecting lines 14 are made from carbon fiber materials. If, for example, the tubular membrane in question is to be used as a fuel cell element or the like, it is possible for some of the threads to be made from an electron-conducting material and for others of the threads to be made from an ion-conducting material. Moreover, the thread system with the ion-conducting action can be provided with a catalyst layer, which can additionally be provided with hydrophobing agents and/or proton conductor material. It is also possible for the described tubular membrane to be used as a bipolar ion-exchange membrane in order to obtain lactic acid or the like. The electrical charge potential of the tubular membrane can also be defined by using metals wires as the thread system.

In the present case, the tubular body 10 consists of eight connecting lines 14 and of eight transverse connection surfaces 16. However, tubular bodies 10 consisting of six connecting lines 14 and six transverse connections 16 have proven particularly advantageous (not shown here). The minimum requirement for constructing a tubular body 10 of triangular cross section (not shown here) is that it be constructed from three connecting lines 14 and three transverse connections 16.

In order for the tubular body 10 constructed in this way to be coated now with a membrane-activatable substance, it is guided through a precipitation bath, the substance being converted into a microporous

membrane layer. A method of this kind is disclosed, for example, in WO 03/076055 A1, so that this will not be dealt with in any more detail here. The known solution according to the WO publication concerns a method for production of fabric-reinforced capillary membranes, particularly for ultrafiltration, in which a fabric tube is in each case coated with a polymer solution and guided through a precipitation bath, the polymer solution being converted into a microporous layer in the precipitation bath. In this way, a membrane that is reinforced by the fabric tube is formed. The fabric tube coated with the polymer solution passes through the precipitation bath from top to bottom, without mechanical contact, and exits through a nozzle at the bottom. Liquid flows out through the nozzle and exerts a tensile force on the capillary membrane leaving the precipitation bath and thus stabilizes the course of the coated fabric tube. The coating method in question is given only as an example, and there are many other coating methods that can be used here, including immersion bath methods. The membrane material is chosen from the group of synthetic materials such as polyethersulfone (PES), polysulfone (PSU), polyacrylonitrile (PAN) or polyvinylidene fluoride (PVDF).

The tubular membrane according to the invention can be produced continuously and therefore inexpensively, that is to say the tubular body 10 is prepared on a permanent basis by the crocheting method for the subsequent coating method with the membrane material 18. By virtue of the filter material being made in the form of a conductive knit or circular conductive knit by use of the conventional crocheting technique, a filter tube is obtained in which the longitudinal tensile stresses arising during filtration are taken up by the continuous longitudinal threads along the fillet-like connecting lines 14, the stresses at the periphery being taken up safely by the transverse

threads 12 of the composite fabric by way of the planar transverse connections 16. The looping at the intersection points (balls 22) reduces shifting of the threads 12 relative to one another, so that undesired stretching effects both in the longitudinal direction and in the transverse direction of the tubular body 10 during coating with the membrane material are minimized to a large extent, and the fabric-reinforced filtration capillary withstands very high internal pressures and longitudinal tensioning during filtration. The thread strength here can be obtained using threads 12 with a diameter of 20 to 200 µm, and the thread number along the lines 14 is preferably three to six.

Practical tests have shown that, with comparable dimensioning, and using the selected technical solution in the form of a circular conductive knit, tensile strengths of 100 N/mm^2 can be achieved with an elongation at tear of 1 to 5% and, in the dynamic pressure test, such tubes easily withstand a bursting pressure of ca. 30 to 60 bar, while a shortening of the tube of only 1% is noted, so as to guarantee that the membrane tube according to the invention, designed as a circular conductive knit, is securely retained in a holding device, in particular in the form of at least one module (not shown) of a complete filtration installation.